

INTERACTIONS BETWEEN SOLVENT COMPONENTS, MOLECULAR HYDROGEN AND MINERAL MATTER DURING COAL LIQUEFACTION

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INTRODUCTION

In direct coal liquefaction, the principal objective is to stabilize the molecular fragments generated by the thermal degradation of coal. Preferably, this is achieved by capping the coal-derived free radicals with hydrogen. In turn, this requires that hydrogen is provided at a rate and in a form compatible with the demand established by the thermal reaction of the coal.

Although the ultimate source of hydrogen is hydrogen gas, the most effective route for hydrogen transfer is by way of the liquefaction solvent. Hydrogen is supplied most readily from hydrogen donor compounds which generally are replenished by catalytic reactions (either externally or internally). In the absence of an adequate concentration of active donors, free radicals can be stabilized by other reactions between solvent components and coal (1).

Extensive studies have been carried out in this laboratory to examine the mechanisms of coal liquefaction in both donor and non-donor solvents. The ultimate aims of this research are to provide means of identifying and controlling the optimal recycle solvent composition in a given process.

In earlier reported work (2) certain polycondensed aromatics were identified as effective non-donor coal solvents. These compounds react with molecular hydrogen during coal liquefaction forming low concentrations of active donors, in situ. The process can be catalyzed by coal mineral matter components. In addition, it is considered that the ability of these components to effectively disperse the coal liquefaction products also contributes to their efficacy.

It is recognized that the study of single model compounds, while affording useful information, does not take into consideration the more complex situation in a real solvent where solvent-solvent interactions undoubtedly occur (1). As a first approach to this problem, the previous studies have been extended to investigate coal conversion in a binary solvent system consisting of a conventional donor (tetralin) and polycondensed aromatics. The results of these investigations are presented below.

EXPERIMENTAL PROCEDURE

Experiments were conducted with bituminous (Monterey) and sub-bituminous (Belle Ayr) coals. The coals were prepared from 1-2" diameter lumps which had been stored under an argon atmosphere (without drying) in a refrigerated room since sampled from the mine. The lumps were crushed and sieved to minus 100 mesh in a glove bag under flowing argon. When sufficient sample had been ground, it was thoroughly mixed and then sealed in small vials, still under argon. A different vial was used for each experiment, the required quantity of coal being weighed from a newly opened vial and the remainder discarded. Analyses of the prepared coals are shown in Table 1.

The conversions were carried out in a small stirred autoclave which has been described in detail elsewhere (1). Essentially this is a reactor of about 12 cc. capacity heated by a close fitting electric furnace. Agitation is provided through the movement of an oscillating plunger which is driven by an electromagnet. A relatively large free volume above the reactor is

kept cold which acts as a gas reservoir allowing operation under virtually isobaric conditions.

The reactor was loaded with a mixture of solvent and coal in the ratio of 3:1 on a dry coal basis. After pressurizing the reactor, the system was heated to the desired temperature with agitation. The time required to reach reaction temperature was an additional 30 minutes. Reproducibility of temperature profiles was good as were the calculated conversions. Several sets of repeated experiments showed a variation of less than $\pm 3\%$ in conversion.

At the end of the reaction, a quantity of tetrahydrofuran (THF) was injected into the reactor while still under pressure following which it was quenched using an ice/water bath. The objective of injecting THF was to facilitate the removal of the solid reaction products (e.g. when pyrene was the solvent) from the reactor.

After venting, the reactor contents were removed in more THF and transferred to a Soxhlet extraction thimble where they were continuously extracted in THF for 18-24 hrs under argon. Conversions were calculated on the basis of the insoluble residue.

The soluble products were analyzed by gas chromatography and GC/MS.

RESULTS AND DISCUSSION

Experiments were carried out to investigate the dissolution of Belle Ayr and Monterey coals in mixtures of pyrene with tetralin and 2-methylnaphthalene with tetralin. The effects of donor concentration, gas atmosphere and hydrogen pressure on coal conversion and hydrogen transfer from tetralin were determined. In addition, some experiments were conducted to examine the reactions between pyrene, tetralin and hydrogen gas.

Coal Conversions

Conversion to THF soluble products and gases is shown as a function of tetralin concentration for Belle Ayr and Monterey coals in Figures 1 and 2 respectively. The reactions were carried out at 400°C for 1 hr under 1000 psig gas pressure. On the two figures, data are presented showing conversions in pyrene-tetralin mixtures both in argon and in hydrogen and, for comparison, in 2-methylnaphthalene-tetralin mixtures in the presence of hydrogen.

For both coals, the conversion in the absence of a donor was enhanced by the presence of gaseous hydrogen. As has been shown (2), the conversion obtained in pyrene is higher than in a less condensed compound such as 2-methylnaphthalene and its effectiveness as a solvent is related to the formation of dihydropyrene during liquefaction.

With reference to Figure 1, the effect of adding tetralin up to about 8 wt% appeared to have little effect on conversion in the three systems shown. Further increase in the donor concentration was accompanied by increasing conversion which reached a limiting value of about 85% at tetralin concentrations of about 70% and above. At the high donor levels, the conversion was not

apparently affected by the nature of the other component or by the gas atmosphere. The major differences between the solvent systems are evident at tetralin concentrations between 8-70%.

From the Figure it is apparent that hydrogen gas is beneficial. However, at a given tetralin level methylnaphthalene based solvents with hydrogen show only a modest improvement over pyrene based solvents without hydrogen. In marked contrast pyrene based solvents respond dramatically to hydrogen pressure and at only 30% tetralin, the blended solvent is almost as effective as 100% tetralin.

The same general effects are observed for the conversion of Monterey coal, Figure 2. In this instance, the two lower curves are not parallel. However, the conversion in 2-methylnaphthalene shows approximately proportional dependence on tetralin concentration whereas in the pyrene-tetralin-H₂ system there is again a major increase in conversion with as little as 15% tetralin.

It has previously been reported that the presence of molecular hydrogen can increase coal conversion in solvents which have low donor capacity (3). The data presented here confirm these findings and also demonstrate that the effect of hydrogen gas is dependent upon the chemical structure of the other compounds present. In particular, the combination of a polycondensed aromatic (pyrene) with a donor in the presence of hydrogen behaves synergistically with respect to coal conversion.

Effect of Hydrogen Pressure

The influence of hydrogen pressure on the conversion of the two coals is shown as a function of donor concentration in Figure 3. The pressures examined were 1000 and 1800 psig.

There was no apparent effect due to hydrogen pressure, over this range, for the conversion of Belle Ayr coal. However, with Monterey coal, the effect of increasing pressure was to increase the conversions in pure pyrene and to some extent, in pyrene-tetralin mixtures to that obtained in pure tetralin. From the standpoint of maximizing conversion of Monterey coal, at high hydrogen pressure, there is little benefit to be derived from the addition of tetralin. This is not to state that the quality of the liquefied products is independent of donor concentration.

The effects of hydrogen pressure during coal conversion have been reported for the Exxon EDS process when operating in a mode where vacuum tower bottoms were recycled (4). Such a recycle stream would be expected to contain a proportion of polycondensed aromatics and compounds with similar chemistry. It was found that increasing the hydrogen pressure from 1500 to 2500 psig gave improved conversion and improved selectivity to lighter products for a range of coals including ones similar to those reported here.

The different responses of the two coals studied here may be partly attributable to differences in their respective mineral matter compositions. It has been

reported that the hydrogenation of pyrene is related to the coal pyritic iron content (2) which is much higher for the Monterey coal.

Hydrogen Transfer

It is commonly known that the extent of coal conversion is related to the hydrogen consumed in the process. Under given reaction conditions, the quantity of hydrogen required is independent of solvent composition. At any given time, the majority of hydrogen is supplied by the most labile source.

It may be assumed that, in the systems described, tetralin is the preferred hydrogen source. For each experiment, the amount of hydrogen made available by tetralin dehydrogenation was calculated, correction being made for isomerization to methylindan. It was found that in the pyrene-tetralin-H₂ system, less hydrogen was made available by tetralin dehydrogenation than in pure tetralin for a comparable conversion level. At lower tetralin concentrations in the mixed solvents, it does not appear that the amount of tetralin was a limiting factor since its dehydrogenation to naphthalene was always less than 40%. Supporting this contention earlier studies (1) have shown that a variation of tetralin concentration from 4 to 43 wt% in Monterey coal conversion, resulted in similar conversions but with corresponding tetralin dehydrogenations of 86 to 8% respectively.

The relative effect of the other solvent component and the gas atmosphere on hydrogen transfer from tetralin is shown in Figure 4 for both coals at a selected level of conversion. In these examples, the tetralin concentration differs since, as shown on Figure 1 and 2, the required concentration to attain a particular conversion is dependent upon the other system components. It can be seen that the required donor capacity for coal conversion is dependent upon the nature of the coal and of the other components present. The implication is that there is considerable potential for economy in donor consumption by judicious control of the solvent composition.

From the previous work with pyrene alone (2) it seems probable that the reduced hydrogen transfer from tetralin is due to part of the hydrogen demand being met by the transfer of molecular hydrogen to the coal through the formation of dihydropyrene. Such a mechanism is not as readily available with 2-methylnaphthalene as it is more difficult to reduce with hydrogen. There was no evidence of the presence of 2-methyltetralin in the reaction products where 2-methylnaphthalene was used as a solvent component.

Thermal Reaction of Pyrene and Tetralin

Some experiments were conducted to investigate the reactions between pyrene, tetralin and hydrogen gas in an attempt to elucidate reasons for the observed synergism. The results are summarized in Table 2 and show the extent of pyrene hydrogenation under the different conditions studied.

It can be seen that pyrene was thermally hydrogenated by reaction with hydrogen gas and under these conditions, its conversion to dihydropyrene was low (0.6%). The extent of hydrogenation was increased by the addition of iron pyrites. These findings are consistent with previous results relating conversion in pyrene to coal mineral matter catalysis (2).

In an inert atmosphere, in the presence of tetralin, 5.7% of the pyrene was hydrogenated. This result is particularly significant as it establishes that tetralin can transfer hydrogen to pyrene producing a substantial concentration of a more active donor. The same experiment conducted under molecular hydrogen resulted in a still greater degree of pyrene hydrogenation which was higher than would be predicted from a purely additive effect.

The foregoing results suggest that there may be several different mechanisms to effect H-transfer in systems which contain donors and polyaromatic compounds. Some possible alternatives are discussed below.

Neglecting direct interaction of hydrogen gas with coal derived free radicals, there appear to be four possible routes for H-transfer:

- 1) Tetralin + R → Naphthalene + R-H
- 2) Tetralin + Pyrene → Naphthalene + Dihdropyrene
- 3) Pyrene + H₂ → Dihdropyrene
- 4) Dihdropyrene + R' → Pyrene + R-H

Reaction 1) is the conventionally regarded process of hydrogen transfer from a donor. Reaction 2), it has been shown, can take place thermally and is promoted by molecular hydrogen. Reaction 3) can occur thermally and is catalyzed by coal mineral matter. Reaction 4) is parallel to reaction 1) and presumably proceeds at a faster rate.

In pure tetralin, reaction 1) prevails and in pure pyrene, reactions 3) and 4) take place. In pyrene-tetralin mixtures under hydrogen, all four reactions are possible and on this basis an explanation for the observed synergism in conversion and for the reduction in hydrogen transferred from tetralin is proposed.

The combined effect of reactions 2) and 3) is to generate a higher concentration of dihydrodropyrene than when 3) alone is possible. Dihdropyrene would be preferred to tetralin as the hydrogen donor since it has been shown that depletion of donors is essentially sequential (1). That is, until the most active donor is reduced to a low level, there is little significant contribution from the next most labile hydrogen source.

The ensuing increase in dihydrodropyrene concentration due to H-transfer from a low concentration of tetralin, especially in the early stages of reaction, could account for the observed synergism. In addition, some of the net hydrogen demand will be met via reaction 3) which will reduce the amount of hydrogen which otherwise would be predominantly supplied by the tetralin. It is anticipated that economies in donor concentration and consumption observed in these model compound studies would be observed in a process such as EDS when operating with bottoms recycle.

This explanation is tentative and there are many other factors which have not been considered, among which are the differences in solubility and dispersive properties of pyrene and tetralin and their mixtures. The outcome of these studies shows that there are potential advantages to coal liquefaction through an improved understanding of solvent chemistry which can lead to the selection and control of solvent composition. Some benefits of selected solvent recycle have already been observed in practice (4, 5, 6) and improvements such as those found in these model compound mixtures could significantly affect the viability of a coal liquefaction process.

SUMMARY

Studies of coal conversion in mixtures of pyrene, 2-methylnaphthalene and tetralin have shown that:

- 1) Mixtures of pyrene and tetralin in the presence of hydrogen gas have been found to be synergistic in coal conversion. At tetralin concentrations as low as 15 wt%, the conversion was almost as high as that in pure tetralin.
- 2) There is no similar synergistic effect when 2-methylnaphthalene is substituted for pyrene. The ease of reduction of pyrene is considered to be one reason for this different behavior.
- 3) With pyrene-tetralin mixtures in hydrogen, the hydrogen supplied by the donor at a given level of coal conversion is considerably reduced.
- 4) Reactions between pyrene, tetralin and hydrogen gas in the absence of coal showed that pyrene can be hydrogenated by reaction with molecular hydrogen alone and by tetralin alone. In combination with tetralin and hydrogen, the extent of pyrene hydrogenation is further enhanced.

ACKNOWLEDGEMENT

This work was conducted under Electric Power Research Institute (EPRI) Contract No. RP-1655 which is jointly funded by EPRI and Mobil Research and Development Corporation. Mrs. L. F. Atherton is the EPRI Project Manager.

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Table 1
Properties of Coals

	<u>Belle Ayr</u>	<u>Monterey</u>
Elemental Analysis (m.f.)		
% C	72.20	75.18
H	5.65	5.82
O	20.56	12.78
N	1.19	1.38
S	0.40	4.34
Ash	4.50	11.19
Sulphur Forms		
Pyritic	0.03	0.68
Sulphate	0.03	0.75
Organic	0.35	2.97
Total	0.41	4.40

Table 2
Thermal Reactions of Pyrene, Tetralin and Hydrogen

Solvent	Gas	Time (mins)	Temp (°C)	Pressure (psig)	% Pyrene Conversion to Dihdropyrene
Pyrene	H ₂	60	400	1000	0.6
92% Pyrene/8% Iron Pyrites	H ₂	60	400	1000	2.5
50% Pyrene/Tetralin	Ar	60	400	1000	5.7
50% Pyrene/Tetralin	H ₂	60	400	1000	8.6

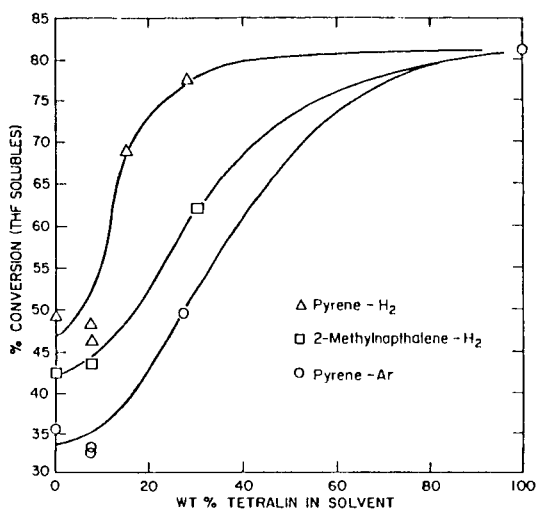


Figure 1. Conversion of Belle Ayr Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

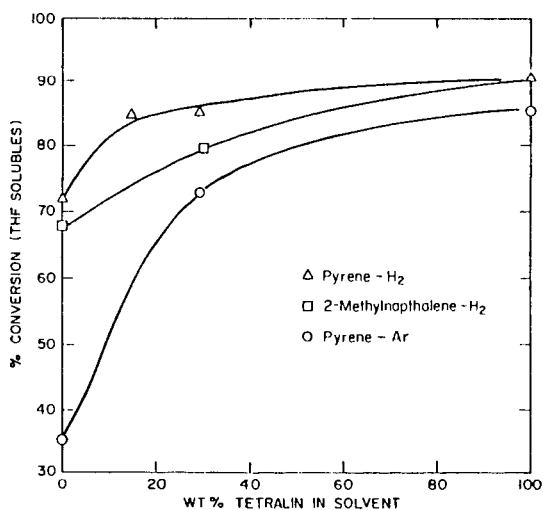


Figure 2. Conversion of Monterey Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

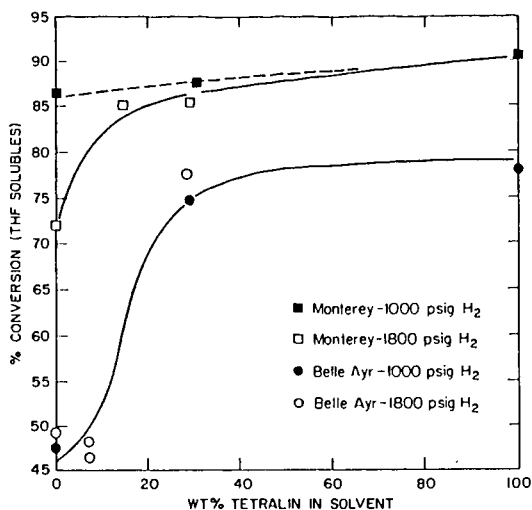


Figure 3. Effect of H₂ Pressure on Coal Conversion in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr)

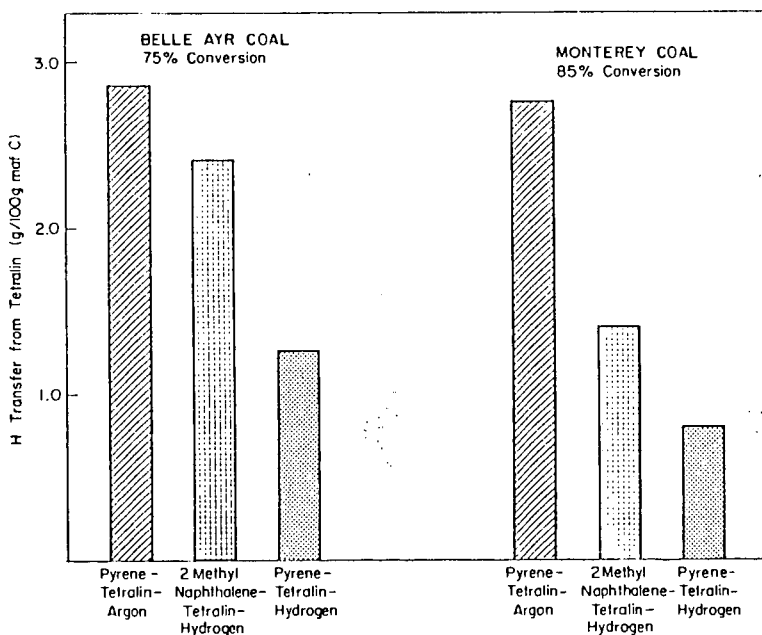


Figure 4. Effect of Solvent and Gas Atmosphere on Hydrogen Transfer (400°C, 1 hr, 1000 psig)